

A process for synthesizing metal borohydrides

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Background of the Invention

This invention relates generally to the field of synthesizing metal borohydrides, and more particularly to a process for synthesizing sodium borohydrides and its alkali solution.

The metal borohydrides especially alkali metal borohydrides such as KBH_4 , LiBH_4 and NaBH_4 are unique compounds in their ability to carry large amounts of hydrogen. They can be stabilized by dissolving into alkali solution. They can release hydrogen gas by the use of catalysts such as Cu, Co, Ni etc if needed. When reacting with water, 1 molar of KBH_4 or NaBH_4 can produce 4 molars of pure hydrogen gas in which 2 molars of hydrogen come from borohydrides and the other 2 molars come from water. The theoretical capacity of hydrogen storage in NaBH_4 is high up to 21wt% because water

also becomes carrier of hydrogen in this case. Therefore, the metal borohydride alkali solutions offer great potential as a fuel in fuel cell systems or any other applications when such effect is desired. In addition, as atoms H in metal borohydrides are -1 value, which has excellent reducing characteristics, therefore, in theory, metal borohydrides especially alkali metal borohydrides should find their applications in almost every field where reducing agent is needed.

The metal borohydrides have not obtained their expected widespread usage simply because of their high costs. As said in US patent No. 3734842, "the selling price of sodium borohydride", a kind of metal borohydrides can be used to further produce other metal borohydrides, "produced in accordance with conventional industrial processes is necessarily pegged to the cost of metallic sodium". The reaction now employed for the production of sodium borohydride in industry as below:



One molar sodium borohydride needs 4 molar metallic sodium in conventional industrial process. This process by the use of metallic sodium to produce metal borohydrides was described clearly in details in the article titled "Na borohydride: Can cost be lowered?", Canadian Chemical Processing, 47, No. 12, 57-59 and 62 (1963) and US patent No. 3473899. US patent No. 3734842, 4931154 and 5804329 described another method to produce metal borohydrides by the use of electrochemical cells. In these kinds of methods, a cathode, an anode and membrane were used and borohydrides were said to be produced from borate ions directly. However, once borate

ions are reduced to borohydride ions, OH^- ions are produced also and then negative borate ions and OH^- ions will be co-existing in electrolyte, whichever the electrolyte is aqueous solution or not, OH^- is prior to borate ions to be produced into water. This will result in a very difficult to further produce borohydride ions and even can be produced; the efficiency of making borohydrides ions will be too low to be practically used in industries. Therefore, in the past 50 years many efforts have been put in trying to reduce the costs of metal borohydrides but by now the production of metal borohydrides in industry scale is still pegged by metallic sodium. Consequently, the costs are still very high.

Summary of the Invention

One object of the invention is to provide a cheaper production of metal borohydrides especially Sodium borohydride by the use of proton H to replace metallic sodium

Another object is to provide a novel method for synthesizing sodium borohydride under ambient temperature and pressure.

A further object of the invention is to provide a novel method for synthesizing sodium borohydride directly from borax but not from $(\text{CH}_3\text{O})_3\text{B}$. This will further reduce the cost of synthesizing metal borohydrides.

Other objects and advantages of the present invention will become apparent from the following descriptions, taken in connection with the accompanying drawings, wherein, by way of illustration and example, an embodiment of the present invention is disclosed.

The invention provides a simple, novel and low cost technology for reducing metal borohydrides especially sodium borohydride directly from borax or NaBO_2 by the use of proton H but not metallic sodium. The metal borohydrides such as but not limited to KBH_4 , NaBH_4 and LiBH_4 are synthesized simply by a mechanical chemical method that contains the following processes:

A. Process of synthesizing the carriers of proton H or the carriers of catalysts for splitting hydrogen gas as proton H.

Mechanically mixing and pulverizing metals such as Mg, V, Zr, Ti, La, Y, Ce, Ca, Nb etc or their alloys with 0-50wt% hydrogen storage alloys such as but not limited to FeTi to make the hydrogen storage alloys locate on the surface of above metal powders.

Mechanically mixing and pulverizing the mixed powders described as mentioned above with 0-100wt% alkali materials such as but not limited to NaOH or KOH.

Surface capillary treatment. Put the powders produced by the above processes under water vapor with 0-1 atm for 0-48 hours. After this process, the surface of the powder should have metallography characteristics shown in Fig.1 and Fig.2.

Or mechanically mixing and pulverizing metals such as Al, Fe, Mg, Zn, V, Zr, Ti, La, Y, Ce, Ca, Nb etc or their alloys with 0-10wt% Pt or Pd coated carbon black to

make the Pt or Pd coated carbon black locate on the surface of above metal powders.

B. Process of generating and supplying proton H

Keeping the powders produced from the above processes under 0-50 atm pressure hydrogen gas at from ambient temperature to 400°C for 0-48 hours.

Or by the use of electrochemical or any other methods to produce proton H.

C. Process of synthesizing metal borohydrides

Mechanically mixing and pulverizing non-aqueous metal boron oxides or borax with the powders produced by process A and B under 0-50 atm hydrogen gas existing at ambient temperature to 400°C for 0-48 hours.

D. Process of synthesizing metal borohydride alkali solution or pure metal borohydrides

Add alkali such as but not limited to KOH and NaOH solutions with concentration from 0.5wt% to saturate into the powders produced through the above processes A, B and C.

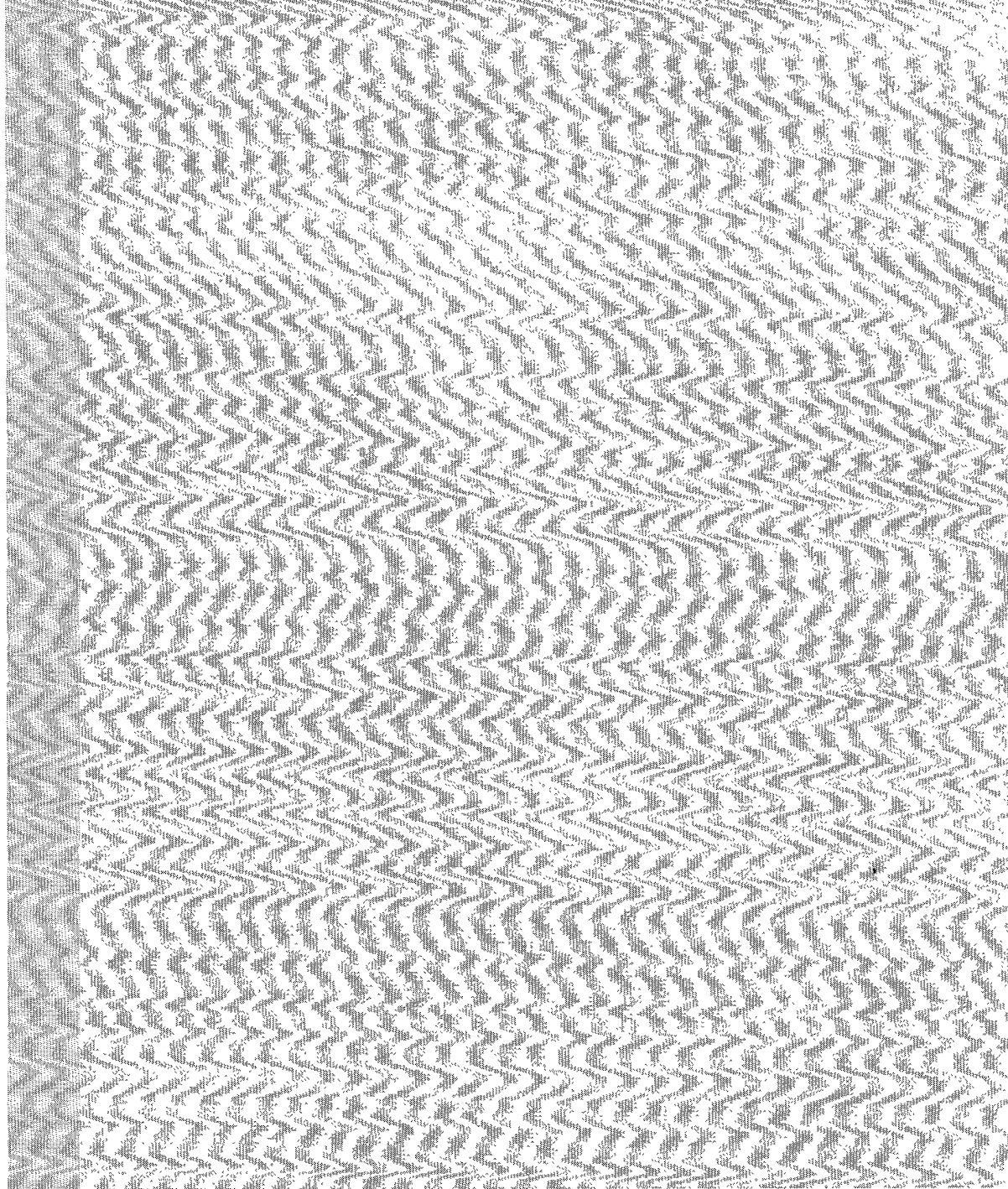
Filter precipitates to obtain metal borohydride alkali solutions.

Or dissolve the powder produced through the above process A, B and C into liquid ammonia or any liquids that can dissolve metal borohydrides

Filter precipitates and evaporate these liquids such as ammonia to obtain pure metal borohydride.

The drawings constitute a part of this specification and include exemplary embodiments to the invention, which may be embodied in various forms. It is to be

understood that in some instances various aspects of the invention may be shown exaggerated or enlarged to facilitate an understanding of the invention.



Detailed Description of the Preferred Embodiments

Detailed descriptions of the preferred embodiment are provided herein. It is to be understood, however, that the present invention may be embodied in various forms. Therefore, specific details disclosed herein are not to be interpreted as limiting, but rather as a basis for the claims and as a representative basis for teaching one skilled in the art to employ the present invention in virtually any appropriately detailed system, structure or manner.

According to the present invention, a process for synthesizing metal borohydride comprising the following 4 steps (using carriers of Mg, Al and FeTi as example):

The first step is a process of synthesizing the carriers of proton H or the carriers of catalysts for splitting hydrogen gas as proton H. In order to synthesize the carries of proton H, the metals that can form hydrides with hydrogen such as Mg is mixed with 0-50wt% hydrogen storage alloys such as but not limited to FeTi or LaNi₅ alloy, then pulverize them mechanically under 0-50atm hydrogen. After this, add 0-100wt% KOH or NaOH into this powder and mechanically pulverized them to ensure the hydrogen storage alloys and KOH or NaOH locate on the surface of, such as but not limited to Mg powder. In other words, after this process the Mg powder is characterized by a special structure in that on the surface there is a Mg-FeTi-NaOH composition layer while in the center, only pure Mg. The structure of carries is shown in Fig.1. After finished this, putting these powders under water vapor with 0-1 atm for surface capillary treatment.

Fig.2 shows the surface characteristics.

By now the carriers have the following properties: (1). The capillary treated surface has excellent affinity for proton H; (2). As hydrogen storage alloys such as FeTi, LaNi₅ etc. have a far lower pressure for taking up hydrogen than Mg, if these carriers of proton H are put into a given pressure hydrogen gas, hydrogen gas molecules will first be absorbed on the surface of carriers by the alloy. The hydrogen gas is then split into proton H to enter the Mg-FeTi-NaOH composition layer to form hydride. Finally the proton H is diffused to enter the lattice of Mg to form MgH₂ hydride. (3) After the carriers fully become hydride, the outer layer of carriers has a saturate proton H concentration because the hydrogen storage alloys located on the outer layer has lower equilibrium pressure of hydrogen than Mg located in center. (4) Because the surface of carriers has good affinity to proton H, the surface proton H will be stable to stay in the Mg-FeTi-NaOH composition layer until we need these proton H to remove the carriers surface by the foreign force.

In order to synthesize the carriers of catalysts for splitting hydrogen gas as proton H, the Pt or Pd coated carbon black is mixed and pulverized mechanically with aluminum or other metals that can form oxides but difficult to form hydrides with hydrogen. After finishing this process, the Pt or Pd coated carbon black will locate on the surface of aluminum. In this case, the surface will be associated with the production of proton H from splitting hydrogen gas molecule.

The second step is the process of generating and supplying proton H in that providing

proton H by the use of metals or alloys that can form hydrides with hydrogen. In this case, the metals or alloys are the carriers of proton H; Or providing proton H from splitting hydrogen gas by the use of catalysts located on the surface of carriers;

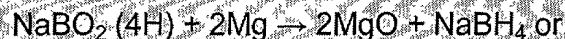
In order to do this, keeping the powders produced from the above processes under 0-50 atm pressure hydrogen gas at from ambient temperature to 400°C for 0-48 hours. In such cases as the carriers of proton H is Mg-FeTi, proton H will be produced by hydrogen storage alloys located on the surface first and then stored in this alloys and center Mg. While in the case such as to use Pt or Pd coated carbon black /Al carriers, proton H will be produced only on the surface and can not be stored in the carriers.

The third step is a process of synthesizing metal borohydrides in that making the proton H enter the lattice of boron oxides and removing the oxygen from the lattice of boron oxides by the use of carriers.

In order do this, mechanically mixing and pulverizing non-aqueous metal boron oxides or borax with the powders produced by the above two processes under 0-50 atm hydrogen gas existing at from ambient temperature to 400°C for 0-48 hours

The above processes can be shown as the following reactions (take NaBO_2 and borax $\text{Na}_2\text{B}_4\text{O}_7$ as examples of the metal boron oxides in this category):





The last step is a process of synthesizing metal borohydride alkali solution or pure metal borohydrides

Just adding alkali such as but not limited to KOH and NaOH solutions with concentration from 0.5wt% to saturate into the powders produced through the above three processes. Filter precipitates to obtain metal borohydride alkali solutions. Or dissolve the powder produced through the above three processes into liquid ammonia. Filter precipitates and evaporate liquid ammonia to obtain pure metal borohydride.

EXAMPLE 1

Mechanically mix 60 g Magnesium powder with 3 g FeTi alloy powder and pulverize them in a closed container under 5-atm hydrogen gas protection for 1 hour. Adding 3 g NaOH into the above container and mechanically pulverize them at the same condition for 1 hour. Vacuum this container first and then pipe water vapor into this container to keep pressure at 0.5 atm for 1 hour. After these steps, the powder has surface characteristics as shown in Fig. 1 and Fig. 2.

Vacuum this container first. Pipe hydrogen gas into this container to keep the pressure at 473K, 50 atm for 24 hours.

Leaking the container to 1atm. Add non-aqueous sodium boron oxide NaBO_2 65.8 g into this container. Mechanically mix and pulverize them at ambient temperature, 5atm hydrogen gas for 3 hours.

Leaking the container to 1atm, open the container and put the powders into 1000 ml 6N NaOH solution to make sure the powders dissolve fully. Filter precipitates and measure the concentration of NaBH_4 dissolved in alkali solution. The results are shown in Table 1.

Table 1

| | |
|---------------------|------|
| NaBO_2 (g) | 65.8 |
| Mg (g) | 60 |
| FeTi (g) | 3 |

| | |
|---|-------|
| Concentration of NaBH_4 (mol/L) | 0.937 |
| Transferring ratio of NaBH_4 (%) | 94 |

EXAMPLE 2

Replace the 65.8g NaBO_2 used example 1 into 60 g $\text{Na}_2\text{B}_4\text{O}_7$, the other conditions are the same as example 1. The results are shown in Table 2.

Table 2

| | |
|---|-------|
| $\text{Na}_2\text{B}_4\text{O}_7$ (g) | 60.0 |
| Mg (g) | 60 |
| FeTi (g) | 3 |
| Concentration of NaBH_4 (mol/L) | 0.642 |
| Transferring ratio of NaBH_4 (%) | 96.3 |

EXAMPLE 3

Mechanically mix 60g aluminum powder with 10 g 10wt% Pt coated carbon black and

pulverizes them in a closed container under 5atm-hydrogen gas protection for 3 hours. Leaking the container to 1atm. Add non-aqueous sodium boron oxide NaBO_2 65.8 g into this container. Mechanically mix and pulverize them at ambient temperature, 50atm-hydrogen gas for 24 hours.

Leaking the container to 1atm, open the container and put the powders into 1000-ml liquid ammonia to make sure they dissolve fully. Filter precipitates and evaporating liquid ammonia, what's left is pure NaBH_4 . The results are shown in Table 3.

Table 3

| | |
|---|-------|
| NaBO_2 (g) | 65.8 |
| Al (g) | 60 |
| Pt-coated carbon (g) | 10 |
| NaBH_4 (g) | 13.38 |
| Transferring ratio of NaBH_4 (%) | 35.4 |

EXAMPLE 4

Replace the 65.8-g NaBO_2 used in Example 3 with 60 g $\text{Na}_2\text{B}_4\text{O}_7$, the other conditions is the same as in example 3. The results are shown in Table 4.

Table 4

| | |
|---|-------|
| $\text{Na}_2\text{B}_4\text{O}_7$ (g) | 60.0 |
| Al (g) | 60 |
| Pt-coated carbon (g) | 10 |
| NaBH_4 (g) | 8.46 |
| Transferring ratio of NaBH_4 (%) | 33.6% |

While the invention has been described in connection with a preferred embodiment, it is not intended to limit the scope of the invention to the particular form set forth, but on the contrary, it is intended to cover such alternatives, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the appended claims.